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[Abstract]

[Object] The object of the present invention is to achieve a high yield of ultra-fine carbon tubes by developing a novel catalyst in a method for manufacturing ultra-fine carbon tubes by a vapor-phase growth process.

[Solution] The present invention provides a method for manufacturing ultra-fine carbon tubes which is characterized by the fact that a hydrocarbon is decomposed at a high temperature on a catalyst consisting of metallic molybdenum or a substance containing metallic molybdenum, and ultra-fine carbon tubes are deposited on this catalyst.

(57) [Claims]

[Claim 1] A method for manufacturing ultra-fine carbon tubes which is characterized by the fact that a hydrocarbon is decomposed at 800 to 1200°C on a catalyst consisting of metallic molybdenum or a substance containing metallic molybdenum, and ultra-fine carbon tubes are deposited on this catalyst.

[Claim 2] A method for manufacturing ultra-fine carbon tubes which is characterized by the fact that said method comprises [a] a hydrocarbon decomposition process in which [i] a hydrocarbon is decomposed at 800 to 1200°C inside a reaction vessel containing a catalyst consisting of metallic molybdenum or a substance containing metallic molybdenum, and [ii] ultra-fine carbon tubes are deposited on this catalyst, and [b] a catalyst discharge process in which the catalyst on which the ultra-fine carbon tubes have been deposited is discharged from the aforementioned reaction vessel.

[Claim 3] A method for manufacturing ultra-fine carbon tubes which is characterized by the fact that a hydrocarbon oil containing a catalyst consisting of metallic molybdenum or a substance containing metallic molybdenum is injected into a reaction vessel maintained at a temperature of 800 to 1200°C, and this hydrocarbon is decomposed.

Detailed Description

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention] The present invention relates to a method for manufacturing ultra-fine carbon tubes known as "carbon nanotubes", etc.

[0002]

[Prior Art] It is known that ultra-fine carbon tubes are present in cathodic deposits produced by an arc discharge in graphite, etc., and manufacturing methods using such an arc discharge, such as the rotating cathode method, etc., have been developed. Furthermore, methods for manufacturing carbon nanotubes by means of a vapor-phase growth process using iron, cobalt or nickel as a catalyst have also been developed. However, in the case of arc processes, temperature control is difficult, so that the product contains large amounts of ultra-fine particles consisting of a graphite impurity, etc. Furthermore, since the manufacturing capacity is correlated with the power consumed per unit cross-sectional area of the cathode graphite, it is difficult to increase the scale of manufacture, and the amount of production per unit time is small. Meanwhile, the amount of production in the case of the vapor-phase growth method is determined by the size of the reaction vessel, the amount of catalyst used and the amount of raw material supplied; accordingly, this method is superior as a large-scale manufacturing method for ultra-fine carbon tubes. An important factor in manufacturing methods using such a vapor-phase

growth process is the catalyst; many studies aiming at the development of more effective catalysts have been conducted.

[0003]

[Problems to Be Solved by the Invention] The object of the present invention is (1) to increase the yield of ultra-fine carbon tubes by developing a novel catalyst, and (2) to develop a method that allows continuous operation and large-scale production, in a method for manufacturing ultra-fine carbon tubes by means of the aforementioned conventional vapor-phase growth process.

[0004]

[Means Used to Solve the Abovementioned Problems] The present inventors perfected the present invention as a result of diligent research conducted with the aim of solving the abovementioned problems. Specially, the present invention provides a method for manufacturing ultra-fine carbon tubes which is characterized by the fact that a hydrocarbon is decomposed at 800 to 1200°C on a catalyst consisting of metallic molybdenum or a substance containing metallic molybdenum, and ultra-fine carbon tubes are deposited on this catalyst. Furthermore, the present invention also provides a method for manufacturing ultra-fine carbon tubes which is characterized by the fact that said method comprises [a] a hydrocarbon decomposition process in which [i] a hydrocarbon is decomposed at 800 to 1200°C inside a reaction vessel containing a catalyst consisting of metallic molybdenum or a substance containing metallic molybdenum, and [ii] ultra-fine carbon tubes are deposited on this catalyst, and [b] a catalyst discharge process in which the catalyst on which the ultra-fine carbon tubes have been deposited is discharged from the aforementioned reaction vessel. Moreover, the present invention also provides a method for manufacturing ultra-fine carbon tubes which is characterized by the fact that a hydrocarbon oil containing a catalyst consisting of metallic molybdenum or a substance containing metallic molybdenum is injected into a reaction vessel maintained at a temperature of 800 to 1200°C, and this hydrocarbon is decomposed.

[0005]

[Working Configurations of the Invention] The catalyst used in the present invention consists of metallic molybdenum, or of a substance that contains metallic molybdenum. Conventionally, catalysts used in the manufacture of ultra-fine carbon tubes (hereafter referred to simply as "tubes") by the decomposition of hydrocarbons have included metallic nickel and metallic cobalt. However, such catalysts are still unsatisfactory in terms of the catalytic activity of the catalysts and the quality of the tubes obtained, etc. In the research conducted by the present inventors, it was unexpectedly discovered that the abovementioned problems can all be solved by using metallic molybdenum as a catalyst.

[0006] The abovementioned substances containing molybdenum (Mo) include inorganic substances containing Mo and organic substances containing Mo. Such inorganic

substances containing Mo include inorganic Mo compounds and systems in which Mo is supported on an inorganic substance, etc.; however, the use of systems in which Mo is supported on an inorganic substance is preferable. Such inorganic substances used to support Mo may include any porous substance that possesses heat resistance; various types of inorganic substances commonly used as catalyst supports may be used. Examples of such inorganic supports include various types of metal oxides such as silica, alumina, magnesia, titania, zirconia and silica/alumina, etc., and various types of clay minerals such as zeolite and sepiolite, etc.

[0007] An ordinary immersion method can be employed as the method that is used to support metallic molybdenum on an inorganic substance. In this method, a molybdenum compound is first dissolved in a solvent (water or an inorganic solvent, etc.) so that a molybdenum-containing solution is prepared. In this case, the molybdenum compound used may be any compound that is soluble in water or organic solvents; for example, molybdenum chloride, molybdenum nitrate or molybdenum acetate, etc., can be used. There are no particular restrictions on the molybdenum concentration in the solution; the upper limit on the concentration is the saturation solubility of the molybdenum compound used. Next, after the inorganic support substance is immersed in this molybdenum-containing solution, the support is dried and fired. In this case, the firing is performed in a hydrogen atmosphere. As a result, a catalyst in which metallic molybdenum is supported on the aforementioned inorganic support substance is obtained. The metallic molybdenum content in this catalyst is 1 wt % or greater, preferably 5 wt % or greater, relative to the total amount of catalyst. There are no particular restrictions on the upper limit of this catalyst content; ordinarily, however, the upper limit is approximately 30 wt %.

[0008] The catalyst of the present invention may also contain other metals such as nickel or cobalt in addition to molybdenum. The catalyst of the present invention can be obtained by subjecting various types of molybdenum-containing catalysts commercially marketed as desulfurizing catalysts to a hydrogen treatment so that the catalytic metal oxide on the support is reduced to a metallic state.

[0009] There are no particular restrictions on the shape of the catalyst consisting of metallic molybdenum or a substance containing metallic molybdenum that is used in the present invention; various shapes may be used. Examples of forms that can be used include powders, pellets, spherical and plate-form catalysts, etc.

[0010] Mo-containing organic substances that can be used in the present invention include chelates and organic acid salts, etc., that contain Mo. Examples of chelates that contain Mo include Mo acetylacetonate, etc.; examples of Mo organic acids [sic] include Mo salts of carboxylic acids, etc.

[0011] In order to manufacture ultra-fine carbon tubes using the method of the present invention, a hydrocarbon is decomposed at a high temperature on the aforementioned catalyst. Various hydrocarbons that are solid, liquid or gaseous at ordinary temperatures may be used as the raw-material hydrocarbon in this case. Examples of such hydrocarbons

include acetylene, methane, ethane, benzene, naphthalene and mixtures of these hydrocarbons (naphtha and light oil, etc.). The decomposition temperature is 800 to 1200°C. As a result of the thermal decomposition of the aforementioned hydrocarbons, the desired ultra-fine carbon tubes (carbon nanotubes) are deposited on the catalyst.

[0012] In order to manufacture ultra-fine carbon tubes with good productivity, it is desirable that the method of the present invention be embodied as a continuous process consisting of [a] a hydrocarbon decomposition process in which [i] a hydrocarbon is decomposed at a high temperature inside a reaction vessel containing the abovementioned catalyst, and [ii] ultra-fine carbon tubes are deposited on this catalyst, and [b] a catalyst discharge process in which the catalyst on which the ultra-fine carbon tubes have been deposited is discharged from the aforementioned reaction vessel. In cases where the present invention is embodied as such a continuous process, the continuous production of ultra-fine carbon tubes is possible. Examples of catalytic beds which are suitable for such working of the method of the present invention include moving beds, fluidized beds and fixed beds, etc. In the case of a moving bed, the catalyst can be extracted from the reaction vessel while the reaction is caused to continue. In the case of a fluidized bed or fixed bed, the catalyst can be extracted from the reaction vessel after the reaction is temporarily stopped. The dimensions of the catalysts used in these catalytic beds are equal to the maximum length of the bed (length in the direction of the long axis); this length is 1 to 20 mm.

[0013] Another desirable working configuration of the present invention is a method in which a hydrocarbon oil containing the abovementioned catalyst is injected into a reaction vessel heated to a high temperature, so that the hydrocarbon is decomposed on the catalyst. In this method, the catalyst on which the tubes are deposited adheres to the bottom part and wall parts of the reaction vessel. After the reaction is completed, this catalyst can be extracted from the reaction vessel and recovered. The catalyst used in this method may be any catalyst that can be dissolved or dispersed in the aforementioned hydrocarbon oil. Examples of such catalysts include metallic molybdenum particles with a mean particle diameter of 5 to 50 nm, Mo-containing inorganic substances with a mean particle diameter of 5 to 100  $\mu\text{m}$ , and oil-soluble Mo chelate compounds, etc.

[0014] The separation of the deposited ultra-fine carbon tubes from the catalyst can be accomplished by chemical methods, physical methods or combined chemical and physical methods. One example of such a method is a method which utilizes the fact that metallic molybdenum will dissolve in acids such as nitric acid, etc., while ultra-fine carbon tubes are relatively insoluble in acids. In this method, the catalyst on which the ultra-fine carbon tubes have been deposited (using metallic molybdenum as a catalyst) is caused to contact an acid, so that only the metallic molybdenum is eluted. Furthermore, other methods that can be used include a method in which an external force such as vibration, etc., is applied to the catalyst so that the ultra-fine carbon tubes deposited on the catalyst are stripped away, and a modification of this method in which a heating cycle consisting of heating and cooling is applied to the catalyst beforehand, or the catalyst is caused to contact an acid

such as nitric acid, etc., in order to facilitate the stripping of the ultra-fine carbon tubes from the catalyst, after which an external force is applied.

[0015]

[Working Examples] Next, the present invention will be described in greater detail in terms of working examples.

[0016] Working Example 1 A quartz tube (internal diameter: 24 mm, length: 100 mm) was used as a reaction vessel. Water cooling jackets were connected to both ends of this vessel; furthermore, a gas introduction tube was connected to the front end of the reaction vessel, and a gas exhaust tube was connected to the rear end of the reaction vessel. Inside this reaction vessel, 100 g of a molybdenum catalyst supported on alumina was set in an alumina dish. The Mo content of this catalyst was 15.2 wt % calculated as  $\text{MoO}_3$ . Furthermore, the particle size of the catalyst was approximately 1.6 mm. Next, this reaction tube was heated to 400°C in an electric furnace, and a hydrogen/nitrogen mixed gas with a hydrogen concentration of 10% used to reduce the  $\text{MoO}_3$  was caused to flow through the reaction tube at flow rate of 10 cc/minute set by means of a flow rate regulating device; afterward, the flow path was switched by means of a three-way cock to an acetylene/nitrogen mixed gas with an acetylene concentration of 10%, and this gas was caused to flow through at a flow rate of 10 cc/minute. After the flow-through of the acetylene/nitrogen mixed gas was initiated, the temperature inside the reaction tube was elevated to 1000°C at the rate of 10°C/minute. A mass analysis of the exhaust gas during this period was performed continuously, so that the progress of the reaction was monitored. When the system was switched to the abovementioned acetylene/nitrogen mixed gas with an acetylene concentration of 10% after the catalyst was reduced by the flow of the 10% hydrogen gas, the hydrogen concentration dropped abruptly (to more or less zero), and the acetylene concentration abruptly increased. Since the hydrogen concentration increased slightly even at 400°C, it was inferred that the acetylene decomposed. When the elevation of the temperature to 1000°C was initiated at the rate of 10°C/minute, the hydrogen concentration increased abruptly as the temperature rose, and in the latter half of this process, an accompanying drop in the acetylene concentration was also seen. At the point in time where the temperature reached 1000°C, the decomposition of acetylene was extremely conspicuous, and the violent generation of soot was apparent to the naked eye. Accordingly, the reaction was stopped, the reaction tube was cooled, and the catalyst was removed. When the deposit on the catalyst was observed with a scanning electron microscope (SEM), the presence of high-quality carbon nanotubes was confirmed.

[0017] Working Example 2 Using the reaction vessel described in Working Example 1, a solution prepared by dissolving 1 g of molybdenum acetylacetonate (a molybdenum-containing organic substance) in 1 liter of benzene was supplied at a feed rate of 1 cc/minute to the reaction vessel, which was set beforehand at a temperature of 1000°C. After approximately 10 minutes, soot began to flow out of the exhaust tube; accordingly, the reaction was stopped, and the reaction tube was cooled. When the reaction vessel was

opened and examined, it was found that large quantities of a soot-form product had accumulated on the walls of the reaction vessel. When the recovered product was observed with a scanning electron microscope (SEM), the presence of high-quality carbon nanotubes was confirmed.

[0018]

[Merits of the Invention] The present invention makes it possible to manufacture high - quality ultra-fine carbon tubes at a high yield, and thus has great industrial significance.